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SPECIFICATION

Detailed Description of the Invention

The present invention relates to the production of synthetic leather which is soft and durable and has a smooth surface and is suitable for shoe leather applications, for clothing applications, and for industrial applications that comprises using a nonwoven fabric as the base fabric and forming a layer of resin on its surface.

Various kinds of synthetic leather having a nonwoven fabric as the base fabric have been produced in the past, but examples that possess both softness and a smooth surface are hardly found. The reason for this is that these are mutually contradictory properties. That is, if a surface resin layer is formed on a soft nonwoven base fabric in order to produce a soft synthetic leather, the surface layer contracts when it solidifies, so strain is produced inside the surface layer and unevenness occurs in the nonwoven fabric owing to that strain at the interface with the surface layer, and as a result of the surface layer solidifying in a rough state, only a synthetic leather that lacks surface smoothness can be produced even though it is soft. On the other hand, if the surface layer is formed on a hard nonwoven base fabric in order to obtain a smooth surface layer, a soft synthetic leather will no longer be obtained.

As a result of various investigations to produce synthetic leather that is soft and durable and also has a smooth surface with the above points in mind, the present inventors discovered that a synthetic leather that is soft and durable and also has a smooth surface can be produced by producing a smooth-surface nonwoven fabric having a 5% modulus of ≥ 2.5 kg/3 cm by shrinking a fibrous mat that contains 10-40% of warm water-soluble polyvinyl alcohol-based fibers per total fiber weight in a moist-heat state while at the same time bonding the fibers to each other, and then fixing this shrunken mat by impregnating it with a binder under conditions such that the aforementioned bonding between fibers is not destroyed, then forming a resin surface layer on the surface of this nonwoven fabric, solidifying and setting this layer, and subsequently extracting and removing the warm water-soluble polyvinyl alcohol-based fibers in the nonwoven fabric structure.

In general, methods such as the following are adopted to form the surface layer of synthetic leathers.

- (1) Fixing the surface layer by evaporation of a volatile substance.
- (2) Fixing the surface layer by plasticizing a plasticizable substance.
- (3) Fixing the surface layer by solidification of solutions and gels.

In each case the surface layer contracts when fixed, so strain is produced by the contraction force, and that has an effect on the surface of the nonwoven fabric, causing roughness in the surface layer. However, when the nonwoven base fabric is sufficiently hard and has enough stiffness to overcome the strain of the surface layer, the generation of roughness is prevented. According to the studies of the present inventors, synthetic leather with a smooth surface layer can be produced by using a smooth-surface nonwoven fabric with a 5% modulus of ≥ 2.5 g/3 cm as the base fabric. A nonwoven fabric having a 5% modulus of ≥ 3.0 kg/3 cm is especially preferred.

However, as indicated above, the base fabric with a high 5% modulus imparts a hard property to the final product. Therefore, this invention is intended to provide the production of a synthetic leather with a low 5% modulus, that is, one that is soft and durable and also has a smooth surface as the final product, by including extractable and shrinkable fibers in the nonwoven fabric that will serve as the base fabric, thereby producing a nonwoven fabric with a 5% modulus higher than the above-mentioned limit, then providing a layer of resin on its surface and fixing that in a smooth state, and finally extracting and removing the soluble shrunken fibers in the base fabric to impart softness to it.

It was discovered that to attain this objective, that is, in order that its initial 5% modulus will be sufficiently high to overcome the strain produced when solidifying the resin surface provided on the surface so that a smooth surface can be formed and sufficient softness can be provided the base fabric while retaining a density suitable for used as the base fabric of synthetic leather after the extraction treatment, it is essential to bond the fibers at the same time as shrinking the fibrous mat and to maintain this state permanently. If the shrinking and bonding of the mat are carried out separately, or even if temporary bonding is effected simultaneously with shrinking but the temporary bonding is destroyed before the permanent bonding and deformation occurs, a base fabric with a high modulus initially cannot be produced, and the final product

clearly lacks softness, and particularly when folded, sharpness is apparent. It was also confirmed that fibers which shrink and contribute to temporary bonding, which can be extracted easily, and which are also inexpensive are most advantageous for use as the fibers of the mat.

In the case of this invention, polyvinyl alcohol based fibers were chosen as fibers that satisfy the above conditions. As is widely known, polyvinyl alcohol based fibers swell in water and exhibit adhesiveness and they are easily dissolved by hot water. With respect to shrinkability, it was not really known how shrinkable they were in a water bath, but it was confirmed that they shrink severely, particularly in hot water near the temperature at which they begin to dissolve. The temperature at which these fibers begin to dissolve referred to in this invention indicates the temperature at which, when 1 g of the fibers are immersed in 100 cc of warm water for 1 min, they begin to dissolve and elute in the water. Table 1 shows the percent dissolution and coefficient of linear contraction of polyvinyl alcohol-based fibers known by the commodity name Kuralon VPB, T-201 2.0 d/51 mm (Kurashiki Rayon K.K.) in a warm water bath. The coefficient of linear contraction was measured after immersing the fibers in a water bath for 1 min and allowing them to dry naturally.

Table 1

Temperature of water bath (°C)	20	30	40	50	55	60	65	70	75	80	85
Percent dissolution (%)	0	0	0	0	0	1	22	60	67	80	100
Coefficient of linear contraction (%)	16	23	30	37	42	47	45	42	—	—	—

As will be recognized from this table, the temperature at which Kuralon VPB 20/51 begins to dissolve is 60°C, and it shrinks rather severely above 40°C and especially around 60°C.

The temperature at which the polyvinyl alcohol-based fibers used in this invention begin to dissolve is preferably from 40°C to about 80°C. These fibers are mixed with other unshrinkable synthetic fibers, semi-synthetic (regenerated) fibers, or natural fibers and integrated in the form of a fibrous mat. The mat may be needle-punched to entangle the fibers. The content of polyvinyl alcohol-based fibers in the mat should be selected in the range of 10-40 wt%. If the content is too low, it will not be sufficient to cause the mat to shrink to a sufficiently high modu-

lus in the next process, and if too high, the percent shrinkage of the mat can be increased, but conversely, the amount of fibers extracted will increase and a dense base fabric will not be obtained. The ideal range is 15-30%.

Next, this fibrous mat is given a shrinking treatment and a temporary bonding treatment at the same time. These treatments are performed by immersing the mat in a water bath and drying or by exposing them to steam and drying. When shrinking with a water bath, it is preferred to exercise care that the bath temperature does not exceed the temperature at which the polyvinyl alcohol-based fibers employed begin to dissolve by more than 15°C. It is thought that polyvinyl alcohol-based fibers, when introduced into a warm-water bath, follow a process in which they first swell and the crystal arrangement collapses, following which the fibers begin to dissolve. It is thought that the fibers experience shrinkage in the process up to partial dissolution. Therefore, below the temperature at which the fibers begin to dissolve, the shrinkage becomes increasingly severe as the temperature rises, but when the temperature exceeds that at which dissolution begins, the time from swelling to dissolution is short and the percent shrinkage declines. Especially if the temperature 15°C or more higher than the temperature at which dissolution begins, not only will sufficient shrinkage not occur, but the fibers will dissolve in a short time, so it will be difficult to attain the anticipated objectives.

Shrinking occurs not only in the water bath, but also continues in the process which follows that if the drying temperature is high. Therefore, when the specified areal shrinkage has been produced in the mat in a warm-water bath, preferably in the temperature range from no more than 15°C above to no more than 20°C below the temperature at which the fibers begin to dissolve, it is desirable to control the shrinkage during drying by squeezing the mat before drying. Also, when the mat is immersed in a low-temperature water bath, one may consider drying the mat at a high temperature so that shrinkage will occur mainly in the drying process. When the mat has been dried, shrinking concludes and the surface of the fibers that has swollen at the same time solidifies and the fibers adhere to each other and become fixed.

The mat may be compressed with a roll press or the like before drying in order to make it more dense, but deformation of the mat during shrinking is undesirable. Therefore, measures such as causing the bath liquid to infiltrate the fibrous mat while applying as little tension as possible so that it floats in the water bath is preferred. One may also consider adding a surfactant

to the water bath in order to speed up the infiltration rate. Thus, when the drying has concluded, the internal strain on the non-shrinkable fibers can be maintained as is and those fibers fixed by temporary bonding. Causing the percent shrinkage of the fibrous mat at this time to be in the range of 20-70% by area is ideal for obtaining a high 5% modulus initially and imparting the desired softness and density to the final product.

It is also possible to use steam in this invention instead of the shrinking and temporary bonding by means of a water bath as described above. The temperature of steam can cause sufficient shrinkage without dissolving the fibers in spite of the fact that it is at a far higher temperature than that at which the polyvinyl alcohol-based fibers begin to dissolve. It is thought that the reason for this may be that the vapor does not supply sufficient moisture to cause the fibers to dissolve completely, and the fibers undergo swelling and crystal collapse gradually to the point of partially dissolving, but dissolution does not proceed beyond that, and it is conjectured that the fibers shrink in this process. After the mat has received the steam treatment, it is then dried and bonded as is. The drying may be accomplished by natural drying. Of course, the percent shrinkage will be limited to the range of 20-70% in area, and by this, a dense mat of stable area is produced.

The fibrous mat that has been shrunk and temporarily bonded by the above processes is next impregnated with a binder to effect permanent bonding. As examples of the binder, synthetic rubbers such as acrylonitrile-butadiene rubber, styrene-butadiene rubber, chloroprene rubber and acrylate rubber, natural rubbers, and synthetic resins such as polyurethane, polyurea, polyvinyl acetate, and polystyrene can be mentioned. This binder may be used in any form such as a solution, emulsion, or dispersion. Also, as the method of impregnation, various well-known methods can be adopted as desired depending on the form of the binder. However, what should be taken into consideration here is that the temporary bonding must not be destroyed during this process, as indicated above. Therefore, a solvent that directly dissolves the polyvinyl alcohol-based fibers must not be used as the solvent or dispersant of the binder. For example, when a binder in emulsion form that uses water as the dispersant is employed, thought must be given to keeping the bath temperature below the dissolution temperature of the polyvinyl alcohol-based fibers so as to prevent the destruction of temporary bonding. The binder is precipitated in the mat by vulcanization, crosslinking, dry solidification, and wet solidification. By this process, the

fibers in the mat are permanently bonded in the state they were in when caused to shrink, and a base fabric with a high 5% modulus along with stiffness due to temporary bonding is obtained.

In order to give a smooth finish to the surface of the nonwoven base fabric with a 5% modulus of ≥ 2.5 kg/3 cm, preferably ≥ 3.0 kg/3 cm, thus obtained, a treatment such as hot pressing, ... [meaning of Japanese *katsuroku* could not be determined], or buffing should be carried out.

A resin surface layer is applied to one side of the high-modulus nonwoven base fabric. This can be formed by applying a coating liquid composed of polyurethane resin, polyamide resin, polyvinyl chloride resin, or other well-known material by calendering, knife coating, or flow coating, etc., and solidifying and fixing it according to the usual methods. To form the surface resin layer in this invention, any means may be employed according to the usual methods. Of course, it is desirable that a porous, moisture-permeable surface layer be formed. By this process, even if the strain due to shrinking is applied to the nonwoven fabric substrate when the surface layer solidifies and sets, the base fabric will have a 5% modulus of ≥ 2.5 kg/3 cm, so roughness will never occur in the surface of the nonwoven fabric. Therefore, the surface layer solidifies and sets very smoothly.

The synthetic leather obtained at this stage still does not possess softness. Therefore, it is introduced to the following extraction process, and the polyvinyl alcohol-based fibers are dissolved and removed by vibration in hot water. Because of this, voids arise in the base fabric where the polyvinyl alcohol-based fibers were, and the other, that is, non-shrinkable, fibers are freed from the temporary bonding. Therefore, the non-shrinkable fibers that were compressed with the shrinking of the polyvinyl alcohol-based fibers become able to move through these voids, but as a whole they are fixed by the binder, so the strain applied to the non-shrinkable fibers remains unchanged. It is assumed that the degree of freedom and the strain possessed by these fibers contribute to the elimination of sharpness and improvement of durability in particular, and thus a synthetic leather which has a smooth resin layer on its surface and which is extremely soft although dense, is not sharp, and, more remarkably, excels in durability, is produced. Moreover, the extraction of the polyvinyl alcohol fibers leaves voids, so the nonwoven base fabric substrate has outstanding breathability, moisture permeability, and hygroscopicity, and a

synthetic leather closely resembling natural leather can be obtained by forming a moisture-permeable layer on the surface layer.

This invention will now be explained by giving practical examples.

Practical Example 1

A laminate web comprising 80 wt% nylon fibers (3.0 d/51 mm) and 20 wt% hot water-soluble polyvinyl alcohol-based fibers (2.0 d/51 mm) (the above-mentioned Kuralon VPB.T-201) and having a basis weight of 100 g/m² was produced. This web was immersed in a 60°C warm-water bath for 1 min and then passed through a mangle and dried at 110°C for 3 min to obtain a fibrous mat having an areal shrinkage of 44%, a thickness of 2.1 mm, and a basis weight of 175 g/m². This mat was bonded by the polyvinyl alcohol-based fibers at the crossing points of the fibers and was stable in area.

Next, the fibrous mat was impregnated with styrene-butadiene rubber latex (Hycar LX-101 manufactured by Nippon Zeon) at room temperature. The amount impregnated was controlled so that the fiber/adhesive ratio after drying would be 50/50 by weight. This was dried at 110°C for 10 min to deposit the adhesive without causing a change in area and was also vulcanized at 120°C.

Next, the surface of the mat was buffed to make it smooth, and a nonwoven basis fabric having a smooth surface, a weight of 300 g/m², and a thickness of 1.0 mm was obtained.

A 22% dimethylformamide solution of polyurethane resin (Paraprene 26S manufactured by Hodogaya Chemical) was applied on one side of this nonwoven fabric and solidified by the wet-solidification method to form a smooth surface layer. Next, this was immersed in 85°C hot water, vibrated to extract and remove the polyvinyl alcohol-based fibers, and dried, and a synthetic leather that was dense and soft and also had a smooth surface layer was obtained. The properties of the nonwoven base fabric before applying the surface layer and of the synthetic leather obtained are shown in Table 2.

Comparative Example 1 in that table indicates the test results for synthetic leather obtained by impregnating a fibrous web consisting only of 3.0 denier/51 mm nylon fibers with the binder and performing a surface treatment and forming a surface layer by the same methods as in Practical Example 1.

Practical Example 2

The same fibrous web as used in Practical Example 1 was needle-punched (needle density: 120/cm) to produce a needled felt weighing 150 g/m^2 . This was immersed in 60°C warm-water for 1 min and dried at 110°C for 3 min after removing the excess moisture to obtain a mat that had been shrunk by 57% in area and become temporarily bonded. This mat was 2.2 mm thick and weighed 340 g/m^2 .

Table 2

	Practical Example 1	Comparative Example 1
Nonwoven base fabric		
Weight (g/m ²)	300	270
Thickness (mm)	1.0	0.9
5% modulus (kg/3 cm)	3.2	1.7
Synthetic leather		
Weight (g/m ²)	390	390
Thickness (mm)	1.4	1.3
5% modulus (kg/3 cm)	1.3	2.2
Surface state	Good	Rough
Sharpness	No	Yes
Flex resistance (times)*	50,000	25,000

*By Bally flexometer

This fibrous mat was impregnated with styrene-butadiene rubber latex at room temperature as in Practical Example 1 (fiber/adhesive \cong 50/50) and dried without causing a change in area, and the adhesive was cured. Next, this mat was buffed to make its surface smooth, and a synthetic leather base fabric was obtained. The properties of this base fabric are shown in Table 3. A surface layer was provided on this base fabric as in Practical Example 1. Next, the extraction treatment was carried out, and the properties of the synthetic leather obtained are shown in Table 3. Comparative Example 2 in this table indicates the test results for a synthetic leather prepared as in Practical Example 2 except for not including polyvinyl-based fibers in the fibrous web used in Practical Example 2.

Table 3

	Practical Example 2	Comparative Example 2
Nonwoven base fabric		
Weight (g/m ²)	520	470
Thickness (mm)	1.1	1.2
5% modulus (kg/3 cm)	4.2	2.3
Synthetic leather		
Weight (g/m ²)	600	600
Thickness (mm)	1.5	1.6
5% modulus (kg/3 cm)	1.8	2.9
Surface state	Smooth	Rough
Sharpness	No	Slight
Flex resistance (times)*	100,000	65,000

(57) Claim

Production of synthetic leather that is soft and durable and has a smooth surface layer which is characterized by shrinking a fibrous mat that contains 10-40% of warm water-soluble polyvinyl alcohol-based fibers per total fiber weight in a wet-heat state and at the same time bonding the fibers to each other, impregnating this shrunken mat with a binder under conditions that do not destroy the above-mentioned bonding between the fibers to produce a nonwoven fabric having a 5% modulus of ≥ 2.5 g/3 cm, giving the surface of this a smooth finish, and then providing a resin surface layer on the surface of this nonwoven fabric structure, solidifying and setting this layer, and then extracting and removing the warm water-soluble polyvinyl alcohol-based fibers in the nonwoven fabric structure.